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**EUROPEAN PATENT APPLICATION**

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㉙ Glass fibre reinforced cementitious products.

㉚ An alkali-resistant mineral fibre for use as a reinforcement in cementitious products and its method of production are disclosed. The method comprises forming a melt having a composition within the range by weight of about 20 to 30% CaO, about 15 to 20% MgO and the balance SiO<sub>2</sub>, at a temperature of about 35 to 100 Celsius degrees above the melting point of the composition, atomizing the melt with high pressure air or steam to form fibres, and cooling the fibres for collection. The melt can be formed from the mineral diopside alone or diopside with at least one of up to 10% by weight of sandstone or quartz and up to 20% by weight dolomite.

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## GLASS FIBRE REINFORCED CEMENTITIOUS PRODUCTS

This invention relates to a mineral fibre composition in the form of filaments or fibres for incorporation as reinforcement into cementitious materials such as cement, mortar or concrete.

5        This use of reinforcement in concrete to improve the strength of concrete structures is well known. For example, structural steel members, steel rods and steel mesh are commonly used to improve the strength and impact resistance of concrete structures used in buildings, bridges, light standards and the like. Asbestos fibres have also been commonly used to reinforce cementitious materials as a replacement for steel reinforcing to reduce the weight of the reinforced structures by incorporating 15-20 weight percent of fibrous asbestos minerals such as chrysotile in a cement matrix. However, asbestos reinforcement is expensive, is no longer desirable because of suspected health hazards, referred to in U.S. Patent 4,153,439, and provides low impact strength with moderate flexural strength.

10       The use of hollow glass spheres, foamed glass or glass fibres produced from slags and the like silicate materials have been used but found generally unsuitable for long term reinforcement of concrete or cementitious products because of general instability in the alkaline environment of hydrating cements. For example, Portland cement attacks and substantially weakens glass fibres precluding long term reinforcement of cementitious products.

United States Patent 4,002,482 issued January 11, 1977 sets forth a number of techniques which have been attempted in order to overcome this situation. For example, the high pH of the cementitious material has been reduced by the use of atmospheric carbon dioxide or by the introduction of carbon dioxide into compacted concrete. This technique has proved too complicated. It has been proposed to coat glass fibres with an alkali-resistant synthetic resin. Adhesion characteristics of coated glass fibres relative to the cement matrix were not satisfactory. A proposal to use highly alkali-resistant glass fibres or spheres did not eliminate the corrosion of the glass and poor adhesion of the glass to a cementitious matrix occurred. Patent 4,002,482 discloses a fibre composite in which a number of metallic oxides are present in a predetermined ratio to produce a glass suitable for long term reinforcing use. Patent No. 2,051,279 discloses the production of rock wool from pyroxenes for uniform chemical composition and colour.

United States Patent 3,408,213 issued October 29, 1963 discloses another embodiment of glass composition suitable for glass fibre manufacture in which the composition contains a number of metal oxides including boron, sodium, calcium and magnesium oxides in predetermined quantities. The production of these glass fibres is expensive.

Canadian Patents 1,018,705; 1,058,459; 1,066,966; and 1,087,773 disclose various coating compositions for glass fibres to reduce their rate of deterioration when incorporated in cementitious materials. Glass fibres treated are continuously drawn fibres preferably having a chemical composition including 5 mole %  $ZrO_2$ , for enhanced alkali resistance.

We have found that a mineral fibre having a composition within the range by weight of about 15 to 20%  $MgO$ , about 20 to 30%  $CaO$ , and the balance  $SiO_2$ , when combined with a cementitious matrix material such as cement, mortar or concrete, surprisingly provides enhanced and long term reinforcement of the resulting cementitious products.

It is commonly believed that mineral fibres suitable for use as a reinforcement in matrix materials must be produced by drawing techniques to attain optimum tensile strength characteristics. It has been found that  
5 mineral fibres produced from starting materials having the above composition by relatively inexpensive atomizing fiberization have good tensile strength characteristics.

More particularly, we have found that the naturally-occurring mineral diopside ( $\text{CaO.MgO.2SiO}_2$ ), alone or  
10 in combination with mineral sources of  $\text{CaO}$ ,  $\text{MgO}$  and  $\text{SiO}_2$ , such as dolomite and sandstone, unexpectedly is particularly suited for the production of mineral fibres having high tensile strength characteristics by the use of atomizing techniques and can be readily incorporated with cementi-  
15 tious materials to provide a reinforcing and alkali-resistant dispersion in the cementitious matrix.

Accordingly, the present invention is directed to mineral fibres for use as a reinforcement in cementitious products and to the method of producing the mineral fibres,  
20 said mineral fibres produced from a starting material having a composition within the range by weight of about 15 to 20%  $\text{MgO}$ , about 20 to 30%  $\text{CaO}$ , and the balance  $\text{SiO}_2$ . The starting material preferably is diopside alone or diopside in combination with up to about 10% by weight  
25 dolomite and/or up to about 20% by weight of a  $\text{SiO}_2$ -bearing material such as sandstone or quartz.

To enhance bending strength and fracture toughness of fibre-reinforced cementitious products, it is preferred to add a coating composition to the fibres. The addition of a  
30 thin coating of hydrophobic material to the fibres before incorporation into the matrix material is believed to increase the strength and toughness of the reinforced product by affecting stress transfer at the fibre-matrix interface such that the fibres are subject to a measure of  
35 pull-out from the matrix and by enhancing the alkaline resistance of the fibres.

The method and product of the invention will now be

described with reference to mineral fibres produced from diopside rock mined in Wakefield, Quebec, having a typical chemical composition of:

	SiO <sub>2</sub>	54.7%
5	CaO	25.5%
	MgO	18.6%
	Na <sub>2</sub> O	0.14%
	K <sub>2</sub> O	0.03%
	Fe <sub>2</sub> O <sub>3</sub>	0.13%
10	Al <sub>2</sub> O <sub>3</sub>	0.6%
	TiO <sub>2</sub>	0.09%
	L.O.I.	0.3%

Crushed diopside rock was fed alone or combined with sandstone at a ratio of about 10:1 or with dolomite at a ratio of about 5:1 for continuous melting in a coke-fired shaft furnace at a temperature in the range of about 35 to 100 Celsius degrees above the melting point of the charge, preferably about 35 to 60 Celcius degrees, e.g. usually at a temperature in the range of 1425 - 1450°C.

20 The sandstone had the following composition:

SiO <sub>2</sub>	98-99%
Al <sub>2</sub> O <sub>3</sub>	0.1%
Fe	0.05-0.1%
Carbonates	Bal.

25 The dolomite had the following composition:

CaO	30%
MgO	20.4%
SiO <sub>2</sub>	3%
Fe	0.4%
L.O.I. (CO <sub>2</sub> )	Bal.

30 The melt was fiberized by impinging the molten stream onto rapidly rotating cylinders and atomizing with high pressure air or steam such that the melt stream was broken into small droplets with long tails. The tails, having 35 lengths up to seven inches if desired, is the wool or fibre

component which was collected with the droplet or "shot" on a moving wire belt to form a blanket. Unacceptable shot was separated from the fibre by passage between granulators comprising opposed, rotating spiked cylinders and the fibres separated from this unacceptable shot at rotating screens.

Example 1

Slag fibres and diopside fibres produced according to the above process were tested for alkaline resistance in accordance with A.S.T.M. Standards for Concrete and Mineral Aggregates, specifically the 1981 Annual Book, Part 14, C-289-81, entitled Standard Test Method for Potential Reactivity of Aggregates (Chemical Method), pages 193-210.

The average value of  $S_c$  (concentration of  $SiO_2$ , millimoles/liter) for slag fibres was an undesirably high 1391, regardless of the value of  $R_c$  (reduction in alkalinity, millimoles/liter). The average  $S_c$  value for diopside fibres was consistently a small negative number. The respective average values, as weight losses, were:

Slag fibres	4.2%
Diopside fibres	Nil

It is thus evident that the diopside fibres had much greater resistance to an alkaline solution than the slag fibres.

Example 2

A set of comparative tests were carried out to show reactivity of E-glass fibres (borosilicate glass fibre), Cem Fil (trade mark of alkali-resistant coated synthetic glass), conventional slag fibres, diopside fibres, diopside-dolomite fibres and diopside-sandstone fibres in alkaline solutions simulated to provide such effects as encountered in hydrating cement. A number of 1 g samples of each material were dispersed in 100 mL of 1N NaOH solution and stirred occasionally at 100°C for 1½ hours,

filtered and washed, and the residue dried at 110°C.

The average percent weight losses were as follows:

	E-glass fibres	1.39
	Cem Fil fibres (A)	0.50
5	(B)	0.46
	Slag fibres	0.86
	Diopside fibres	0.57
	Diopside-sandstone fibres	0.68
	Diopside-dolomite fibres	0.49

10 The diopside fibres and fibres provided by combinations of diopside fibres with sandstone or dolomite had weight losses in the same range as Cem Fil fibres which is commercially used as a cement reinforcement material.

### 15 Example 3

Comparative tests were conducted on an unreinforced control cement, a cement reinforced with diopside fibres, and a cement reinforced with diopside fibres coated with a hydrophobic compound to evaluate bending strength and fracture toughness.

Cement samples were prepared by dispersing the uncoated and coated diopside fibres in cementitious slurries which had the following compositions:

SLURRY COMPOSITION		
25 <u>Material</u>	<u>Control</u>	<u>Diopside (coated and uncoated)</u>
Triton N-57 (trademark)		
(g) surfactant	0.7	0.7
Calcite (g)	66.5	66.5
Cement (g)	94.5	94.5
30 Water (g)	140.0	140.0
Diopside Fibres (g)		30
TOTAL WEIGHT (g)	301.7	331.7

The prepared fibre cement slurries were filtered on a Buchner Funnel. The cakes approximately 9 - 14 mm thick and 12 cm in diameter were removed



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from the funnel, placed under polyethylene sheet for 24 hours, and then cured in water for 3 days and air. dried for 14 days. The central point bending test, span 85 mm, was used to determine the ultimate bending strength. The fracture toughness was measured as an area under the load deflection curve normalized by the cross-sectional area of the specimens.

The results of bending strength and fracture toughness are summarized in the following table.

BENDING STRENGTH AND FRACTURE TOUGHNESS

Material	Bending Strength (MPa)	Fracture Toughness (J/m <sup>2</sup> )
Control (No reinforcement)	4.00 ± 0.85 (n=6)	11.42 ± 4.38 (n=6)
Diopside-uncoated	5.42 ± 0.76 (n=10)	92.17 ± 18.59 (n=5)
Diopside-coated	7.54 ± 0.76 (n=10)	115.50 ± 29.42 (n=5)

The inclusion of fibres according to the present invention, coated and uncoated, as reinforcement in cement, provided an increase in bending strength and a substantial increase in fracture toughness.

The fibres provide long term reinforcement of cementitious materials due to the resistance of the fibres to an alkaline environment and the relative cheaper cost and freedom from health hazards of the fibres renders the diopside fibres a viable alternative as a reinforcement material.

## CLAIMS:

1. A method of producing an alkali-resistant mineral fibre for use as a reinforcement in cementitious products comprising forming a melt having a composition within the range by weight of about 20 to 30% CaO, about 15 to 20% MgO and the balance SiO<sub>2</sub>, at a temperature of about 35 to 100 Celcius degrees above the melting point of the composition, atomizing the melt with high pressure air or steam to form fibres, and cooling the fibres for collection.
2. A method as claimed in Claim 1 wherein the melt is formed from the mineral diopside alone or diopside with at least one of dolomite, sandstone and quartz.
3. A method as claimed in Claim 2 wherein the melt is formed from diopside and up to 10% by weight sandstone or quartz.
4. A method as claimed in Claim 2 wherein the melt is formed from diopside and sandstone having a ratio of diopside to sandstone of 10:1.
5. A method as claimed in Claim 2 wherein the melt is formed from diopside and up to 20% by weight dolomite.
6. A method as claimed in Claim 2 wherein the melt is formed from diopside and dolomite having a ratio of diopside to dolomite of 5:1.
7. A method as claimed in Claim 1 wherein the melt has the composition of about 25% CaO, about 19% MgO and the balance SiO<sub>2</sub>.
8. A method as claimed in Claim 1, 2 or 3 wherein the fibres are dispersed in a cementitious matrix material to form a reinforced concrete product.

9. A method as claimed in Claim 4, 5 or 6 wherein the fibres are dispersed in a cementitious matrix material to form a reinforced concrete product. 0076677

- 5 10. Mineral fibres for use as a reinforcement in cementitious products comprising fibres having the composition of about 15 to 20% MgO, about 20 to 30% CaO and the balance SiO<sub>2</sub>.
- 10 11. Mineral fibres as claimed in Claim 10 in which the fibres are formed from the mineral diopside.
12. Mineral fibres as claimed in Claim 10 in which the fibres are formed from the mineral diopside alone or with  
15 at least one of dolomite, sandstone and quartz.
13. Mineral fibres as claimed in Claim 12 in which the fibres are formed from diopside and up to 10% by weight sandstone or quartz.  
20
14. Mineral fibres as claimed in Claim 10 in which the fibres are formed from diopside and dolomite with a ratio of diopside to dolomite of about 5:1.
- 25 15. Mineral fibres as claimed in Claim 12 in which the fibres are formed from diopside and up to 20% by weight dolomite.
16. Mineral fibres as claimed in Claim 12 in which the  
30 fibres are formed from diopside and sandstone with a ratio of diopside to sandstone or quartz of about 10:1.
17. Mineral fibres as claimed in Claim 11 in which the fibres are formed by melting the mineral diopside in a  
35 furnace at a temperature in the range of about 35 to 60 Celcius degrees above the melting point of diopside and atomizing the diopside melt with high pressure air or steam to form fibres.



European Patent  
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# EUROPEAN SEARCH REPORT

0076677  
Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 82305255.0
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
A	<u>GB - A - 790 397</u> (ACTIEN-GESELLSCHAFT DER GERRESHEIMER GLASHÜTTENWERKE) • Page 1, lines 70-92; page 2, lines 1-13; claims 1,4 • —	1,7	C 03 C 13/00 C 03 B 37/01 C 04 B 31/06
A	<u>US - A - 1 842 772</u> (ZOLTAN VON VERESS) • Page 1, lines 1-3, 56-70 • —	1,7	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 7)
			C 03 B C 03 C C 04 B
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 30-12-1982	Examiner HAUSWIRTH
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosures		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons	